Surface Tension of Aqueous Solutions of Alkanolamines: Single Amines, Blended Amines and Systems with Nonionic Surfactants[1]

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ABSTRACT

We have used the differential capillary-rise and the pendant-drop methods to determine the surface tension of aqueous solutions of diethanolamine (DEA) and methyldiethanolamine (MDEA) in the range 293-363 K, as a function of concentration. We have also studied aqueous blends of DEA and MDEA in the range 313-333 K, at a total concentration of the two amines of 50 wt %, using different MDEA/DEA mass ratios. Furthermore, since foaming is a surface phenomenon that is present in absorption equipment it has to be studied in order to develop sound mitigation techniques through the use of foam inhibitors, thus the surface tension of aqueous DEA 20 mass % has also been studied with the nonionic surfactants Span20, Span60, Span80, and Brij92, at different temperatures, as a function of concentration around their critical micelle concentration (CMC).

Key works: aqueous systems; diethanolamine, methyldiethanolamine, nonionic surfactants, surface tension.

1. INTRODUCTION

Adsorption/desorption of bulk-soluble surfactants onto or out of a fluid interface occurs in two consecutive steps: (i) surfactants molecules diffuse between the bulk phase and the sublayer adjacent to the fluid interface; (ii) surfactant molecules are exchanged between the sublayer and fluid interface through the kinetic processes of adsorption and desorption. The description of these processes and the evaluation of the diffusion coefficient and rate constants are important in understanding the influence of surfactant adsorption on many processes [1].

A surface-active agent (or, more briefly, surfactant) is a substance that, when present at low concentration in a system, has the property of adsorption onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interface free energies of those surfaces or interfaces [2]. Reduction of surface or interfacial tension is one of the most commonly measured properties of surfactants in solution. It depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface (or interfacial) excess concentration of the surfactant, as shown by the Gibbs equation $d\gamma = -\sum_i \Gamma_i \, d\mu_i$.

Nonionic surfactants such as sorbitan fatty acid esters and polyoxyethylene alcohols are widely used in many industrial processes [3]. Several studies [4, 5, 6], on polyoxyethylene alcohols have reported their colloidal properties, such as the critical micelle concentration (cmc), the surface tension at cmc, surface coverage, the salt effect, and the temperature effect, whereas, no data have been reported in the literature for fatty acid esters.

On the other hand, the surface tension of mixtures is an important property for the design of contacting equipment with which some chemical processes are carried out, like gas absorption. Surface tension affects the hydrodynamics and transfer rates of such systems, particularly multiphase systems where a gas-liquid interface exits. Most commercial processes for the bulk removal of CO_2 or H_2S from industrial gaseous streams involve the use of amines, frequently amino alcohols. The most common aqueous amino alcohol solutions are monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP) [7, 8, 9]. MDEA is generally used for the selective removal of H_2S in the presence of CO_2, while DEA is a common solvent for the removal of CO_2. Aqueous solutions containing mixtures of DEA and MDEA, however, are considered to be excellent solvents for the simultaneous absorption of CO_2 and H_2S in situations where a specified amount of CO_2 is to be removed [10]. In general these amines are used in aqueous solutions, and the absorption in mixed amines has specific advantages over the use of single amines [11].

Recently, the use of blended amines (solutions of tertiary + secondary or tertiary + primary amines) has also been proposed [11]. The advantages in this respect include their loading capacity, faster reaction rate, and great savings in energy requirements.

The physical properties of aqueous solutions of DEA, MDEA, and MDEA + DEA + water, such as density and surface tension are necessary for the design of acid gas treatment equipment and for measuring other physical properties such as liquid diffusivities, and gas solubility [12]. Vázquez et al. [13] measured the surface tension of ternary aqueous mixture

MDEA + DEA + water, in the temperature range of 25 °C to 50 ° C. The total amine concentration for the ternary mixture was held constant at 50 mass %, and the MDEA/DEA mass % ratio was varied from 0/50 to 50/0, in 10 mass % steps.

The objective of this work was to measure the density with a densimeter that applies the principle of the vibrating tube, and the surface tension, using the differential capillary-rise and the pendant-drop methods, of solutions of DEA in water in the temperature range 293.15 K to 363.15 K and at 10, 20 and 30 mass % amine; MDEA in water was measured at 323.15 K and at 10, 20, 30, 40 and 50 mass % amine. The ternary system MDEA + DEA + WATER was studied at three differents temperatures in the range 313.15 K to 333.15 K, the total amine concentration for the ternary mixture was held constant at 50 mass % and the MDEA/DEA mass % ratio was varied from 0/50 to 50/0 in 5 mass % steps. The air-solution equilibrium surface tension of nonionic Span20, Span60, Span80, and Brij92 surfactants + aqueous DEA at 20 mass %, has also been studied as a function of concentration, above and below their CMCs.

2. EXPERIMENTAL SECTION

The DEA was obtained from J.T. Baker with a purity greater than 99.9 mol %, MDEA was obtained from Aldrich with a purity better than 99 mol %. The surfactants Span 20 (100 % sorbitan monolaurate), Span 60 (100 % sorbitan monostearate), and Span 80 (100 % sorbitan monooleate) were obtained from ICI Americas Inc., and finally the surfactant Brij92 (polyoxyethylene alcohol) was obtained from Aldrich with a purity greater than 98 mol %. The water was twice distilled and deionized.

2.1. Density. The density measurements for the amines and aqueous solutions + surfactants were carried out with a Sodev 03D vibrating densimeter thermostated by a Heto circulating bath which controlled the temperature within ± 0.003 K, as measured with a H-P quartz thermometer. The densimeter used here applies the principle of the vibrating tube first developed by Kratky et al. [14] which determines the density from the period of oscillation of a tube containing the liquid investigated. The instrument and procedure have been described in the literature [15].

2.2. Differential capillary-rise method. The well-known capillary-rise method, considered to be one of the most accurate absolute methods to study surface tension [16, 17], was used in an all-glass closed cell with three calibrated precision-bore capillaries of different diameters in order to apply the differential capillary-rise method introduced by Sugden [18]. The instrument and procedure have been described in previous work from this Laboratory [19].

2.3. Pendant-drop method. In this case we used a FTA200 dynamic contact angle system. It is built around a rapid video capture of images and automatic image analysis. Measurements are made by observing the drop shape of a fluid which reveals information about the fluid itself or about the surrounding media.

The Laplace-Young equation [16] describes the shape of a fluid drop under equilibrium conditions. A hanging pendant drop can be analysed more reliably than a sessile drop, since one can safely assume axial symmetry for the pendant drop but not for the sessile drop. Figure 1 illustrates a pendant drop.

3. RESULTS AND DISCUSSION

The experimental surface tension data for DEA + water and MDEA + water are tabulated in tables 1 and 2, and also included in figures 2 and 3, respectively. In these systems the surface tension decreases with increasing temperature for any given concentration or mass percent of amine. Our results were compared with those of Rinker et al. [12] and showed an average relative percent error of 0.28 and 0.57, respectively. Tables 1 and 2, and figures 2 and 3 show this comparison.

The experimental surface tension data for MDEA/DEA + water are tabulated in table 3, and also included in figure 4. In this system the surface tension decreases with increasing temperature for any given concentration or mass % ratio of amine. Our results were compared only at two temperatures, i.e., 313.15 and 323.15 K and four mass % ratios (0/50, 30/20, 40/20 and 50/0) with those obtained by Alvarez et al. [20] and showed an average relative percent error of 0.19. At 333.15 K no previous surface tension data have been reported in the literature, that is, surface tension data a this temperature are new.

The experimental surface tension data for aqueous DEA at 20 mass % + Span 20, Span 60, and Span80 in the temperature range 313.15 to 333.15 K are tabulated in tables 4, 5, and 6, and depicted in figures 5, 6, and 7, respectively. The experimental surface tension data for aqueous DEA at 20 mass % + Brij92 in the temperature range 333.15 to 343.15 K are tabulated in the tables 7, 8 and 9, and plotted in figure 8.

In order to confirm that ours surface tension data are highly accurate we employed two different experimentals method to measure the surface tension for aqueous DEA at 20 mass

% + Brij92 in the temperature range 333.15 to 343.15 K. Tables 7 to 8, as well as figure 8, contain the experimental information from both methods. It can be established that the data are of high precision and accuracy.

No previous surface tension data have been reported in the literature for aqueous DEA at 20 mass % + Span20, Span60, Span80, and Brij92.

4. CONCLUSIONS

The surface tension values obtained with the capillary rise method of aqueous DEA agree very well with literature data within an average relative percent error of 0.28, for aqueous MDEA within an average percentage relative error of 0.57. On the other hand, with the pendant drop method, the surface tension of the pure components agrees very well with literature values within an average percentage relative error of 0.02.
The results presented here will be useful for carrying out a complete study on the reduction of foaming in absorption equipment.

ACKNOWLEDGMENTS

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Table 1. Experimental surface tension and density data of aqueous DEA as a function of both concentration and temperature.

Mass % DEA	T/K	ρ/g cm-3	γ/m N m-1 Lit. *	γ/m N m-1 Exp.	R.E %
10	293.15	1.0101	63.90	64.14	-0.37
10	313.15	1.0034	61.74	61.65	+0.14
10	323.15	0.9977		60.69	
10	333.15	0.9941	60.05	60.48	-0.72
10	343.15	0.9886		58.28	
10	353.15	0.9830	56.84	56.49	+0.62
10	363.15	0.9795		55.87	
20	293.15	1.0220	65.27	66.45	-1.81
20	313.15	1.0142	63.31	63.94	-0.99
20	323.15	1.0086		62.62	
20	333.15	1.0052	62.04	61.73	+0.50
20	343.15	0.9991		59.98	
20	353.15	0.9931	58.99	58.38	+1.03
20	363.15	0.9895		57.34	
30	293.15	1.0342	61.94	61.84	+0.16
30	313.15	1.0272	60.17	60.17	+0.23
30	323.15	1.0205		58.57	
30	333.15	1.0170	58.02	57.27	+1.29
30	343.15	1.0104		56.23	
30	353.15	1.0037	55.27	55.01	+0.47
30	363.15	1.0002		53.89	

R.E % = (γLit. - γExp./ γLit.)100

* [12].

Table 2. Experimental surface tension and density data of aqueous MDEA as a function of concentration, at 323.15 K.

Mass % MDEA	ρ/g cm-3	γ/m N m-1 Lit. *	γ/m N m-1 Exp.	R.E %
10	0.9960	55.56	55.68	-0.22
20	1.0047	52.86	52.73	+0.24
30	1.0130	50.42	50.17	+0.49
40	1.0204	48.89	48.18	+1.45
50	1.0269	46.57	46.16	+0.88

* [12].

Table 3. Experimental surface tension of MDEA +DEA +Water as a function of temperature at different ratios mass % MDEA/mass % DEA, at a total concentration of the two amines of 50 mass %.

	mass % MDEA/mass % DEA								
T/K	0/50	5/45	15/35	25/25	30/20	35/15	40/10	45/5	50/0
313.15	54.67	53.77	52.34	50.52	49.86	49.17	48.44	48.14	47.59
323.15	53.04	52.70	51.01	49.49	48.38	47.95	47.26	46.34	45.86
333.15	52.68	51.54	49.90	47.63	46.95	46.52	46.20	45.91	45.40

Table 4. Experimental surface tension of aqueous DEA at 20 mass % + surfactant, at 293.15 K.

Mass % surfactant	γ/m N m^{-1}		
	Span20	Span80	Span60
0	66.45	66.45	66.45
0.3	32.1	33.89	48.71
0.5	31.06	31.63	42.66
1	30.22	30.45	39.6

Table 5. Experimental surface tension of aqueous DEA at 20 mass % + surfactant, at 313.15 K.

Mass % surfactant	γ/m N m^{-1}		
	Span20	Span80	Span60
0	63.94	63.94	63.94
0.3	27.01	31.00	32.09
0.5	26.27	30.22	31.96
1	26.23	30.02	29.07

Table 6. Experimental surface tension of aqueous DEA at 20 mass % + surfactant, at 333.15 K.

mass % surfactant	γ/m N m^{-1}		
	Span20	Span80	Span60
0	61.73	61.73	61.73
0.3	25.89	30.58	31.95
0.5	25.46	29.75	30.53
1	25.27	28.29	29.94

Table 7. Experimental surface tension of aqueous DEA at 20 mass % + brij92, at 323.15 K.

Concentration Mol dm^{-3}	Pendant drop γ/m N m^{-1}	Capillary rise γ/m N m^{-1}	R.E %
0.0000092	29.46	29.49	-0.10
0.000019	28.00	28.18	-0.64
0.000025	27.96	27.79	0.61
0.000051	27.51	27.51	0
0.0001	27.22	27.14	0.29
0.00015	27.05	27.03	0.07
0.0002	27.46	27.47	-0.03

Table VIII. Experimental surface tension of aqueous DEA at 20 mass % + brij92, at 333.15 K.

Concentration Mol dm^{-3}	Pendant drop γ/m N m^{-1}	Capillary rise γ/m N m^{-1}	R.E %.
0.0000092	28.56	28.67	-0.38
0.000019	27.38	27.58	-0.73
0.000025	27.31	27.36	-0.18
0.000051	27.01	27.12	-0.41
0.0001	26.93	26.99	-0.22
0.00015	26.91	26.92	-0.04
0.0002	26.96	26.91	0.18

Table 9. Experimental surface tension of aqueous DEA at 20 mass % + brij92, at 343.15 K.

Concentration Mol dm^{-3}	Pendant drop γ/m N m^{-1}	Capillary rise γ/m N m^{-1}	R.E %
0.0000092	27.68	27.75	-0.25
0.000019	26.86	26.88	-0.07
0.000025	26.85	26.69	0.59
0.000051	26.7	26.63	0.26
0.0001	26.52	26.51	0.04
0.00015	26.42	26.41	0.04
0.0002	26.85	26.69	0.59

FIGURE CAPTIONS

Fig. 1. Pendant drop parameters.

Fig. 2. Experimental surface tension of aqueous DEA as a function of temperature and concentration. Data from this work and from the literature.

Fig. 3. Experimental surface tension of aqueous MDEA as a function of concentration at 323.15 K. Data from this work and from the literature.

Fig. 4. Experimental surface tension of MDEA + DEA + Water as a function of temperature at different ratios mass % MDEA/mass % DEA, at a total concentration of the two amines of 50 mass %.

Fig. 5. Experimental surface tension of aqueous DEA at 20 mass % + surfactant, at 293.15 K.

Fig. 6. Experimental surface tension of aqueous DEA at 20 mass % + surfactants, at 313.15 K.

Fig. 7. Experimental surface tension of aqueous DEA at 20 mass % + surfactants, at 333.15 K.

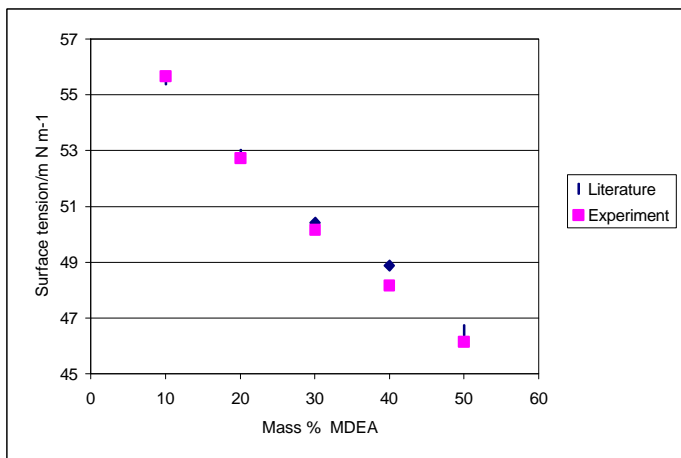Fig. 8. Experimental surface tension of aqueous DEA at 20 mass % + Bri92 as a function temperature and concentration of surfactant.
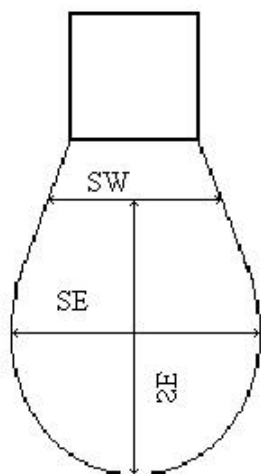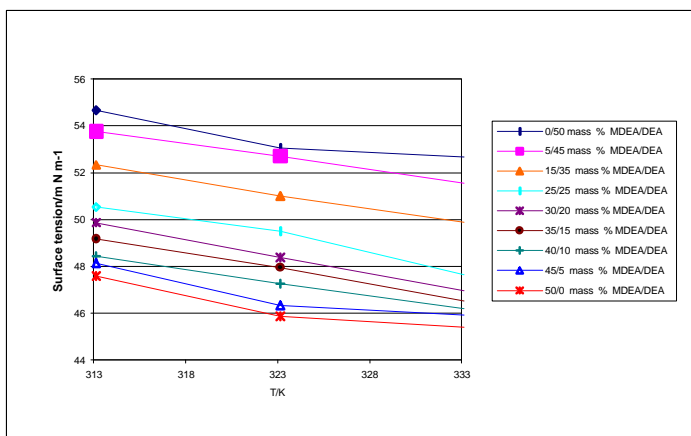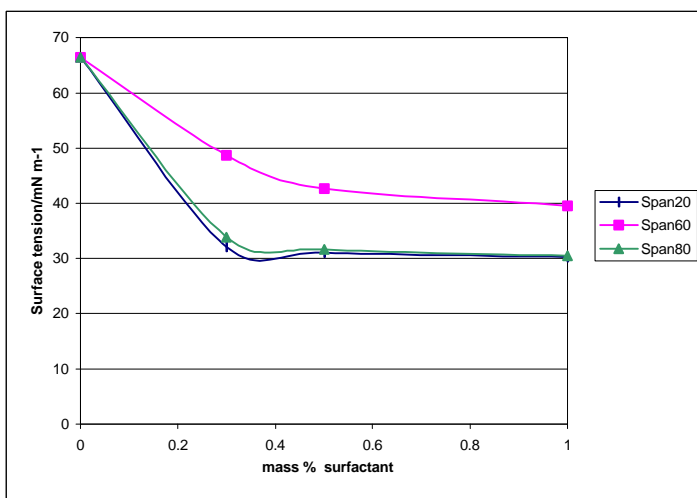
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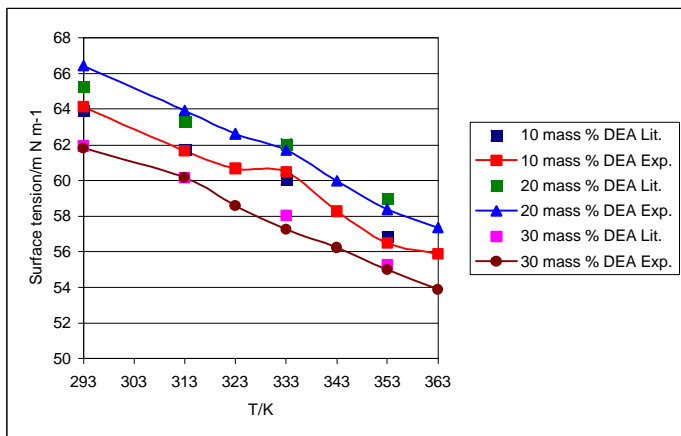
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